

# Angle-resolved photoemission spectra of graphene from first-principles calculations

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## Abstract

Angle-resolved photoemission spectroscopy (ARPES) is a powerful experimental technique for directly probing electron dynamics in solids. The energy vs. momentum dispersion relations and the associated spectral broadenings measured by ARPES provide a wealth of information on quantum many-body interaction effects. In particular, ARPES allows studies of the Coulomb interaction among electrons (electron-electron interactions) and the interaction between electrons and lattice vibrations (electron-phonon interactions). Here, we report *ab initio* simulations of the ARPES spectra of graphene including both electron-electron and electron-phonon interactions on the same footing. Our calculations reproduce some of the key experimental observations related to many-body effects, including the indication of a mismatch between the upper and lower halves of the Dirac cone.

In ARPES experiments a sample is illuminated by monochromatic photons, which can extract electrons from the sample if the photon energy exceeds the work function. Analysis of the kinetic energy and angular distribution of the emitted electrons yields the binding energy of the electron in the material and its crystal momentum parallel to the surface<sup>1</sup>. The measured intensity  $I(\mathbf{k}, \omega)$ , where  $\mathbf{k}$  and  $\omega$  are the momentum and the binding energy of electrons (usually referenced to the Fermi energy), can be written as<sup>1</sup>

$$I(\mathbf{k}, \omega, \hat{e}_\nu, \hbar\nu) = I_0(\mathbf{k}, \omega, \hat{e}_\nu, \hbar\nu) f(\omega) A(\mathbf{k}, \omega), \quad (1)$$

where the function  $I_0(\mathbf{k}, \omega, \hat{e}_\nu, \hbar\nu)$  takes into account the absorption cross section of the incident photon of energy  $\hbar\nu$  and polarization  $\hat{e}_\nu$ . The function  $f(\omega)$  is the Fermi-Dirac distribution, and  $A(\mathbf{k}, \omega)$  is the electron spectral function<sup>1</sup>. In interpreting ARPES measurements in a narrow energy range, it is appropriate to assume that the absorption cross section of the photon is constant. Under these conditions, a measurement of the ARPES spectrum provides direct access to the electronic spectral function  $A(\mathbf{k}, \omega)$ . Within quantum many-body theory the electronic spectral function can be expressed as

$$A(\mathbf{k}, \omega) = \frac{2}{\pi} \frac{-\text{Im}\Sigma(\mathbf{k}, \omega)}{[\omega - \varepsilon_{\mathbf{k}} - \text{Re}\Sigma(\mathbf{k}, \omega)]^2 + [\text{Im}\Sigma(\mathbf{k}, \omega)]^2}, \quad (2)$$

where the  $\varepsilon_{\mathbf{k}}$ 's are the the single-particle energy eigenvalues of a reference mean-field system, and the self-energy  $\Sigma(\mathbf{k}, \omega)$  accounts for the many-body interactions going beyond the mean-field picture<sup>1</sup>. For simplicity of discussion, the band indices are dropped from Eq. (2) (see Methods).

In our investigation, we use density-functional Kohn-Sham eigenstates to describe the mean-field or non-interacting electrons. The electron self-energy arising from the  $e$ - $e$  interaction  $\Sigma^{e-e}(\mathbf{k}, \omega)$  is evaluated within the  $G_0W_0$  approximation<sup>2</sup> (Fig. 1a). This corresponds to retaining the first diagram in the Feynman-Dyson perturbation expansion of the self-energy operator but in terms of the screened Coulomb interaction  $W_0$  (Supplementary Discussion 3 for a comparison with previous first-principles calculations<sup>3,4</sup>). In this work,  $G_0$  is constructed from the Kohn-Sham eigenvalues and eigenfunctions of density-functional theory, and  $W_0$  is the bare Coulomb interaction screened by the full frequency-dependent dielectric matrix  $\epsilon(\mathbf{r}, \mathbf{r}', \omega)$  calculated within the random phase approximation. The self-energy  $\Sigma^{e-\text{ph}}(\mathbf{k}, \omega)$  arising from the  $e$ - $\text{ph}$  interaction is similarly evaluated within the Migdal approximation<sup>5</sup> (Fig. 1b). With these choices, the  $e$ - $e$  interaction and the  $e$ - $\text{ph}$  interaction are

described consistently within the same level of approximation<sup>6</sup> (see Methods). The total self energy is then obtained as

$$\Sigma(\mathbf{k}, \omega) = \Sigma^{e-e}(\mathbf{k}, \omega) + \Sigma^{e-\text{ph}}(\mathbf{k}, \omega). \quad (3)$$

Graphene, a single layer of carbon atoms in a honeycomb structure, has recently become an active research area in physics, chemistry, and nanoscience not only because of its peculiar low-energy massless Dirac fermion band structure<sup>7-9</sup>, but also because it holds promise for novel electronics and spintronics applications<sup>10</sup>. In particular, the epitaxial growth of graphene on silicon carbide (SiC) has emerged as one of the promising routes towards large-scale production of graphene<sup>9,10</sup>.

The interpretation of the measured ARPES spectra of epitaxial graphene grown on silicon-rich surface of SiC has been controversial. The spectral features observed in early ARPES measurements<sup>11</sup> were interpreted qualitatively in terms of *e-e* and *e-ph* interactions. On the other hand, experiments and analyses performed by a different group suggested that the low-energy ARPES spectrum is dominated by a quasiparticle energy gap of 0.2-0.3 eV at the Dirac point<sup>12</sup>. According to Ref.<sup>12</sup>, this band gap likely arises from the coupling of the graphene layer with the reconstructed surface of the SiC substrate. Despite a number of subsequent studies to resolve this controversy<sup>13,14</sup>, the detailed nature of the low-energy quasiparticle dynamics in epitaxial graphene remains an open question.

The electronic structure and the photoemission spectra of graphene have also been explored in a number of theoretical investigations using density-functional theory approaches within a non-interacting single-particle picture<sup>15-17</sup>. The effects of many-body interactions have also been investigated in model calculations<sup>18,19</sup>. However, first-principles calculations of the full  $\mathbf{k}$ - and  $\omega$ -dependent ARPES spectral function - which contains both the quasiparticle dispersions and their lifetimes - including the *e-e* and the *e-ph* interactions have not been reported. The lack of first-principles many-body investigations can partly be ascribed to the extremely demanding computational efforts required to evaluate the real part of the electron self-energy, both for the *e-e* and for the *e-ph* contributions.

In dealing with effects of *e-e* interactions, first-principles calculations have advantages over model calculations based on the two-dimensional massless Dirac equation<sup>18,19</sup>. First, the scattering rate of even the low-energy charge carriers, whose non-interacting dispersion relation can be well approximated by the two-dimensional massless Dirac equation, shows

strong wavevector-anisotropic behaviors<sup>20</sup>. This is because the carrier scattering rate in graphene depends sensitively on the sign of the band curvature<sup>21</sup>. Therefore, the significant wavevector anisotropy in the electron scattering rate is not captured by the model calculations. Second, the model calculations require a cutoff of the high-energy states and an adjustable parameter mimicking effects of internal screening arising from the high-energy states (including the  $\pi$  states higher in energy than the cutoff and the  $\sigma$  states), in addition to the external screening due to the environment. The first-principles approach employing the full bandstructure accounts for these processes explicitly and requires neither a high-energy cutoff nor an empirical parameter to describe the internal screening.

To determine the quasiparticle energy vs. momentum dispersion relations from the calculated ARPES intensity maps for graphene (Figs. 2a, 2d, and 2g), we follow the standard procedure adopted in analyzing ARPES experiments<sup>1</sup>. First, the energy distribution curves (EDCs) are obtained by performing cuts of the intensity maps at fixed photoelectron momentum (vertical cuts in Figs. 2a, 2d, and 2g). Subsequently, the quasiparticle band structures are generated by connecting the locations of the maxima in the EDCs for each photoelectron momentum (Figs. 2b, 2e, and 2h). This procedure ensures that the calculated and the measured dispersion relations are obtained from the corresponding intensity maps using the same procedure.

While the dispersion relations extracted from our spectral functions for an isolated graphene layer are linear at large binding energy, we observe a sizable kink for  $n$ -doped graphene near the Dirac point ( $\mathbf{k} = 0$  in Fig. 2) at an energy below the Dirac point energy. Such kinks result in a mismatch between the linear extrapolations of the lower and the upper portions of the Dirac cone (Fig. 2). A similar phenomenon has been observed in the measured ARPES spectra<sup>11,12</sup>. In order to quantify the size of the kinks and the associated energy mismatch, we have taken the energy difference between the two linear asymptotes of the upper and the lower bands ( $\Delta_{\text{kink}}$  in Fig. 2f). This calculated energy offset  $\Delta_{\text{kink}}$  is predominantly a result of many-body effects, which comes from the  $GW$  self-energy, and is found to increase with the doping level (see Fig. 3), consistent with the experimental trend<sup>11</sup>. We have checked that, if many-electron effects are not considered, the energy mismatch is several times smaller, with value  $\leq 20$  meV for the most heavily doped case considered here and even smaller for other cases. We note that, for the path along which the ARPES spectra are calculated (inset of Fig. 2c), the nonlinearity of the bare graphene band is smallest.

Although the calculated  $\Delta_{\text{kink}}$  shows qualitative agreement with experiment, after taking into account the screening of the SiC substrate (Refs.<sup>18,19</sup>, see Methods), our calculated values underestimate the experimentally observed offsets in Ref.<sup>11</sup> consistently by 60-90 meV; this discrepancy, together with the comparison between theory and experiment of electron linewidths discussed in Ref.<sup>20</sup> and later in this paper, suggests the possible opening up of a band gap at the Dirac point energy due to the interaction between graphene and a reconstructed silicon-rich surface of SiC<sup>12,15-17</sup>. Our study shows the need of further first-principles studies, considering both the atomistic structure of the graphene-substrate interface and many-body effects.

The quasiparticle velocity can be extracted from the simulated spectral functions. We find that  $e$ - $e$  interactions greatly enhance the band velocity by over 30 % compared to the density-functional theory value in pristine graphene, but dielectric screening from the SiC substrate (by weakening the  $e$ - $e$  interaction) reduces the quasiparticle velocity by as much as  $\sim$ 10 % (Supplementary Discussion 1 and Fig. 5). Moreover, the calculated velocity decreases with doping (Fig. 5) in agreement with previous calculations<sup>4</sup>.

Our calculations also reveal phonon-induced kinks near the Fermi energy at binding energies between 150 and 200 meV (e.g., Fig. 4a) in good agreement with experimental photoemission maps<sup>11-14</sup>. These signatures of the  $e$ - $\text{ph}$  interaction in graphene have been analyzed thoroughly both experimentally and theoretically<sup>22-25</sup>.

A complementary and important piece of information provided by ARPES intensity maps is the linewidth of the electronic quasiparticle peaks. The linewidth  $\Gamma_{n\mathbf{k}}$  is related to the lifetime  $\tau_{n\mathbf{k}}$  of the electron in a given quasiparticle state through  $\tau_{n\mathbf{k}} = 2\hbar/\Gamma_{n\mathbf{k}}$ , and plays an important role in transport phenomena. The electron linewidths are extracted from the measured photoemission spectra by considering momentum distribution curves (MDCs), which are constant-energy cuts of the intensity maps. The width of the MDC at a given binding energy can subsequently be obtained using a Lorentzian fit<sup>1</sup>. From our simulated ARPES spectra of graphene along the  $\Gamma$ KM direction in wavevector space (Fig. 4a), we obtained the MDCs (Fig. 4b) and their widths (Fig. 4c). Unlike previous methods<sup>20</sup>, this procedure is direct and is not confined to materials having a linear electronic dispersion.

The widths extracted from the calculated MDCs in  $n$ -doped graphene after including the effect of the SiC substrate screening (see Methods) follow closely the experimental measurements on epitaxial graphene at large binding energies<sup>11</sup>, although they underestimate

the experimental data close to the Dirac point energy (Fig. 4c). The agreement between calculated and measured widths at large binding energy and the underestimation of the linewidths close to the Dirac point energy provide additional support to the proposed scenario of a band gap opening arising from the interaction with the SiC substrate<sup>12,15–17,20</sup>. That is, the opening of a band gap and the generation of midgap states near the Dirac point energy (not included in our calculations) would lead to increased linewidths in this energy regime<sup>17</sup>. However, from the view point of theory, a conclusive statement can be made only after first-principles calculations considering both the atomistic structure of the graphene-substrate interface and the many-body effects, which is beyond the scope of this work.

The widths extracted from the calculated full ARPES spectrum and those obtained by calculating the imaginary part of the on-shell electron self-energy  $\text{Im } \Sigma(\mathbf{k}, \varepsilon_{\mathbf{k}})$ <sup>20</sup> are similar for  $n$ -doped graphene with the same charge density. (The charge density of  $n$ -doped graphene considered in Ref.<sup>20</sup> is different from that in Fig. 4.) However, it is important to note that the current method of using the full ARPES spectra, although involving heavier computations, is more powerful because it can be in general applied to systems whose bare electronic energy dispersion is not linear.

In this work, the effects of substrate optical phonons have not been considered. These substrate phonons contribute to the room-temperature transport properties of graphene<sup>26</sup>. However, over a 1.5 eV range around the Fermi level in doped graphene relevant to ARPES experiments<sup>11,12</sup>, the imaginary part of the electron self energy that arises from interactions with the substrate phonons is less than 1 meV<sup>27</sup>, about two orders of magnitude smaller than the self-energy effects intrinsic to graphene itself<sup>20</sup>.

The present work shows that first-principles simulation of ARPES spectra based on a quantum many-body theory approach treating  $e$ - $e$  and  $e$ - $\text{ph}$  interactions on the same footing holds great potential for the interpretation of complex ARPES spectra. In particular, a direct calculation of the quasiparticle spectral function is needed to obtain meaningful comparisons with experimental data (e. g., the extraction of EDCs, MDCs, linewidths, and quasiparticle dispersion relations).

## Methods

## 1. Computational setup

The Kohn-Sham eigenstates of graphene are obtained using density-functional theory calculations within the local density approximation (LDA)<sup>28</sup> in a supercell geometry<sup>29</sup>. Electronic wavefunctions in a  $72 \times 72 \times 1$  k-grid are expanded in a plane-waves basis with a kinetic energy cutoff of 60 Ry. The core-valence interaction is treated by means of *ab initio* norm-conserving pseudopotentials<sup>30</sup>. Graphene layers are separated by 8.0 Å and the Coulomb interaction is truncated to prevent spurious interaction between periodic replicas<sup>31</sup>. We have checked that increasing the interlayer distance to 16.0 Å makes virtually no difference in the calculated self energy. Charge doping is modeled by an added electron density with a neutralizing background.

Extending the procedure presented in Ref.<sup>20</sup>, where only the imaginary part of the on-shell electron self-energy  $\text{Im}\Sigma^{e-e}(\varepsilon_{\mathbf{k}})$  arising from electron-electron (*e-e*) interactions is calculated ( $\varepsilon_{\mathbf{k}}$  being the LDA energy eigenvalue), we calculate the full frequency dependence of both the real and the imaginary parts of the dielectric matrix (within the random phase approximation) and the self-energy operator  $\Sigma^{e-e}(\omega)$  within the  $G_0W_0$  approximation in the present work. Thus our theory includes the two scattering mechanisms arising from *e-e* interaction effects discussed in previous model calculations performed within the massless Dirac equation formalism<sup>18,19</sup>, i. e., electron-hole pair and plasmon excitations. Since our calculations are based on first-principles, they are parameter free for suspended graphene and can give information that depends on atomistic details, e.g., the effects of trigonal warping. For convergence of the real part of  $\Sigma^{e-e}(\omega)$ , we have included conduction bands with kinetic energy up to 100 eV above the Fermi level. The frequency dependent dielectric matrix  $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$  is calculated within the random phase approximation using the LDA wavefunctions on a regular grid of  $\omega$  with spacing  $\Delta\omega = 0.125$  eV<sup>32</sup>, and the dielectric matrix at energies in between frequency grid points is obtained by a linear interpolation. In the calculation of the polarizability, for numerical convergence, an imaginary component of magnitude  $\Delta\omega$  of 0.125 eV is introduced in the energy denominator. Convergence tests showed that the dimension of the dielectric matrix may be truncated at a kinetic energy cutoff of  $\hbar^2 G^2 / 2m = 12$  Ry. Additionally, we obtain the electron self-energy arising from electron-phonon (*e-ph*) interactions  $\Sigma^{e-\text{ph}}(\omega)$  following Ref.<sup>23</sup> for different levels of doping.

In our approach, we describe the *e-e* and the *e-ph* interactions within the same level of approximation. Previous studies suggested the use of the quasiparticle dispersions renor-

malized by the  $e$ - $e$  interaction to compute the  $e$ -ph interaction<sup>33</sup>. This latter procedure (not adopted here) would correspond to including some of the higher order processes in  $\Sigma^{e-\text{ph}}(\omega)$  whilst neglecting them in  $\Sigma^{e-e}(\omega)$ , and would result in an unbalanced evaluation of  $e$ - $e$  and  $e$ -ph effects according to different levels of approximation. In any event, even if some  $e$ -ph matrix elements calculated after renormalizing the bands through the  $GW$  approximation were 20% to 40% larger than those used in this work<sup>33</sup>, the band velocity would also be enhanced by a similar factor (this work and Refs.<sup>3,4</sup>), and the two factors would cancel out approximately in the calculation of  $\Sigma^{e-\text{ph}}(\omega)$  [cf. Eq. (2) of Ref.<sup>22</sup>]. Therefore, we estimate that the effects of such alterations on our results are not significant.

## 2. Angle-resolved photoemission spectra

First, the trace of the spectral function with respect to band index  $n$ , i.e.,  $A(\mathbf{k}, \omega) = c \sum_n A_{nn}(\mathbf{k}, \omega)$ , is calculated. Here,  $c$  is a normalization constant,  $|n\rangle$  are the Kohn-Sham eigenstates, and

$$A_{nn}(\mathbf{k}, \omega) = \frac{2}{\pi} \frac{-\text{Im} \langle n\mathbf{k} | \Sigma(\omega) | n\mathbf{k} \rangle}{[\omega - \varepsilon_{\mathbf{k}} - \text{Re} \langle n\mathbf{k} | \Sigma(\omega) | n\mathbf{k} \rangle]^2 + [\text{Im} \langle n\mathbf{k} | \Sigma(\omega) | n\mathbf{k} \rangle]^2}. \quad (4)$$

To simulate the measured angle-resolved photoemission spectra from the calculated spectral functions, we multiplied the spectral function by the Fermi-Dirac distribution  $f(\omega)$  [Eq. (1) of the manuscript] with  $T = 25$  K at which the experiments were performed<sup>11,12</sup>. Then, to take into account the experimental resolutions in energy and momentum, we have convoluted the intensity maps with a two-dimensional Lorentzian mask with  $\Delta k = 0.01 \text{ \AA}^{-1}$  and  $\Delta\omega = 25 \text{ meV}$ , corresponding to the experimental resolution<sup>11,12</sup>. (This convolution results in finite linewidths even for zero binding-energy states.) In simulating the photoemission spectra along the  $\Gamma$ KM direction (Fig. 4a of the manuscript), we have used only one branch of the two linear bands in order to simulate the matrix element effects in  $I_0(\mathbf{k}, \omega, \hat{e}_\nu, E_\nu)$  [Eq. (1) of the manuscript] (cf. Fig. 2 of Ref.<sup>11</sup>). In calculating the width of momentum distribution curves (the linewidths in Fig. 4c), we have arbitrarily subtracted off a constant from the simulated widths so that the width vanishes at zero binding energy, as also done in the analysis of experimental data in Ref.<sup>11</sup>.

## 3. Substrate screening

To include the effects of the dielectric screening associated with the silicon carbide (SiC) substrate, we have, as done in previous studies<sup>11,18,19</sup> (Supplementary Discussion 2 and Fig. 6),

renormalized the bare Coulomb interaction by an effective background dielectric constant  $\epsilon_b = (1 + \epsilon_{\text{SiC}})/2$ , where  $\epsilon_{\text{SiC}}=6.6$  is the optical dielectric constant of silicon carbide<sup>20</sup>; one takes the average of the vacuum dielectric constant and the substrate dielectric constant because graphene is sandwiched in between the two media<sup>34</sup>. Along the lines of Ref.<sup>11</sup>, we do not take into account atomistic interactions between graphene and the reconstructed surface of the silicon carbide substrate<sup>15–17</sup>.

## Supplementary information

### 1. Velocity renormalization

Our simulated spectral functions allow us to study the velocity of Dirac fermions in the linear regime (away from the Dirac point) as a function of dielectric screening of the substrate and doping (Fig. 5). The band velocity of our model epitaxial graphene [ $\epsilon_b = (1 + \epsilon_{\text{SiC}})/2 = 3.8$ ] is found to be smaller than that of suspended graphene ( $\epsilon_b = 1$ ) by as much as  $\sim 10\%$  (Fig. 5). In addition, the velocity decreases as doping increases (Fig. 5), in agreement with the previous calculation<sup>4</sup>. Both trends are easily explained by observing that the polarizability of the substrate and the additional electrons in the graphene layer both lead to weaker *e-e* interactions.

### 2. Substrate dielectric function

In this section, we show that the dielectric function of silicon carbide (SiC)  $\epsilon^{\text{SiC}}(\mathbf{q}, \omega)$  is well represented by the value at  $\mathbf{q} = 0$  and  $\omega = 0$  (i. e., the optical dielectric constant) as far as our calculation is concerned. We also estimate that an error in the electron self energy arising from this simplification is less than 10%.

In calculating the imaginary part of the self-energy, the relevant energy scale of the dielectric function of SiC is the quasiparticle energy measured from the Fermi surface, since the lifetime is determined by the real decay processes to lower energy states [see, e. g., Eq. (5) of Ref. 35]. The energy argument of the inverse dielectric function used in the calculation of the imaginary part of the self energy at energy  $\omega$  varies between  $\omega$  itself and the Fermi energy due to the two Heaviside functions. As long as the dielectric function is reasonably constant over this range, the results are valid. Since we are only interested in the value of the linewidth for states from the Fermi level down to about 2.5 eV below it (as measured

by experiment and presented in Figs. 2 and 4 of the main manuscript), we have checked the validity of our approximation on substrate screening within this energy range and the corresponding wavector range as discussed later. The real part of the self energy is affected by the dielectric screening involving large wavevectors; however, the contribution coming from larger wavevector scatterings is smaller because the Coulomb interaction decreases with  $q$ . The error in the real part of the self energy arising from the inaccuracy in the dielectric function for a larger wavevector would be smaller than that involving a smaller wavevector, which is estimated below.

In order to give a quantitative estimate of the possible error arising from the frequency and wavevector dependence of the dielectric function, we performed first-principles calculations of the dielectric function of 3C-SiC showing dielectric responses very similar to 6H-SiC<sup>36</sup>, which is the substrate used in experiments<sup>11,12</sup>. (The unit cell of 3C-SiC is much smaller than that of 6H-SiC though.)

Supplementary Fig. 6 shows that using the optical dielectric constant ( $\omega = 0$ ,  $\mathbf{q} = 0$ ) is a good approximation for the energy and wavevector regime considered in our work: the maximum variation in the dielectric function is 15%. (We have also checked that the inverse dielectric function shows similar behaviors.) Moreover, since (i) the self energy is an average of many contributions, and, (ii) the finite frequency and finite wavevector effects increase and decrease the value of the dielectric function, respectively, the combined error coming from our approximation will be less than 10%.

Supplementary Fig. 6 also shows (difference between solid and dashed lines) that in fact the maximum anisotropy in the dielectric function of SiC is  $\sim 3\%$ . (We have also checked that the inverse dielectric function shows similar behaviors.) Since the self energy is an average of all contributions, we expect that the anisotropy in the calculated electron self energy arising from that in the dielectric function of SiC will be even smaller than that.

### 3. Comments on other calculations

First-principles calculations of the real part of the self-energy in graphene arising from  $e\text{-}e$  interactions within the  $GW$  approximation have been reported previously<sup>3,4</sup>. The authors of Ref. 4 calculated the frequency dependence of the dielectric matrices within the generalized plasmon-pole model. The authors of Ref. 3 calculated the full frequency dependence of the dielectric matrices using the random phase approximation as we did for the present work.

For consistency we compare our calculations to the latter study.

Our calculated velocity ( $1.23 \times 10^6$  m/s) in suspended graphene is  $\sim 9\%$  larger than the one reported in Ref. 3 ( $1.12 \times 10^6$  m/s). Moreover, unlike the finding of Ref. 3, we do not observe a kink in the quasiparticle band structure of suspended pristine graphene at an energy  $\omega \sim -0.15$  eV when *e*-*ph* interactions are not included. The fact that we observe a gradual increase in the band velocity when approaching the Dirac point energy, rather than a kink at a finite energy value is in line with results of model analytical calculations<sup>21,37</sup>. To clarify this difference, we observe that, in the case of graphene, electronic states with wavevectors on nearest neighboring grid points of a discretized  $N \times N$  mesh of the full Brillouin zone have an energy difference  $\Delta E$  (eV)  $\approx 20/N$ . The Brillouin zone sampling adopted in Ref. 3 ( $10 \times 10$  points) corresponds to electronic eigenstates with minimal energy separation of approximately 2 eV. We find that this energy resolution is not sufficient to achieve convergence in the dielectric matrices needed for the GW self energy (we used instead a  $72 \times 72$  grid, corresponding to energy separations of about 0.25 eV). Therefore we suggest that the difference between the band dispersions and velocities calculated here and those of Ref. 3 may arise from the insufficient Brillouin zone sampling adopted in that work.

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FIG. 1: **Diagrams included in the calculated electron self-energy  $\Sigma$ .** **a**, Electron self-energy  $\Sigma^{e-e} = iG_0W_0$  arising from  $e$ - $e$  interactions within the  $G_0W_0$  approximation.  $G_0$  is the Green's function for bare electrons and  $W_0$  is the screened Coulomb interaction. **b**, Self-energy  $\Sigma^{e-\text{ph}} = ig^2G_0D$  arising from  $e$ - $\text{ph}$  interactions within the Migdal approximation. Here,  $g$  is the  $e$ - $\text{ph}$  interaction matrix element and  $D$  is the dressed phonon propagator.

FIG. 2: **Simulated ARPES spectra, energy distribution curves (EDCs) and quasiparticle band structures of suspended graphene including  $e$ - $e$  and  $e$ - $\text{ph}$  interactions.** **a**, Simulated ARPES spectrum of pristine graphene at  $T = 25$  K taken along the Brillouin zone segment indicated in the inset of **c**. **b**, EDCs extracted from **a**. The central red curve corresponds to  $k = 0$  (the K point). **c**, Quasiparticle band structure (solid red curve) obtained by connecting the peak positions of EDCs in **b**. **d** to **f**, and **g** to **i**, Same quantities as in **a** to **c** for  $n$ -doped graphene with charge densities of  $4.5 \times 10^{13} \text{ cm}^{-2}$  and  $1.2 \times 10^{14} \text{ cm}^{-2}$ , respectively. The dashed blue lines in **c**, **f**, and **i** indicate the asymptotes of the linear bands far from the Dirac point. The energy difference between the upper and the lower asymptotes close to the Dirac point is indicated by  $\Delta_{\text{kink}}$ .

FIG. 4: **Momentum distribution curves (MDCs) of graphene and associated linewidths.** **a**, Simulated ARPES spectrum of suspended  $n$ -doped graphene, for a doping level corresponding to a charge density of  $4.5 \times 10^{13} \text{ cm}^{-2}$ , taken along the Brillouin zone segment indicated in the inset of **c**. **b**, MDCs obtained from **a**. **c**, Width of the MDCs obtained from **b** for suspended graphene (red curve) and that for graphene with a model dielectric screening corresponding to the SiC substrate (blue curve). The measured widths of the MDCs<sup>11</sup> are shown for comparison (black curve).

FIG. 3: **Mismatch between the upper and lower bands of the Dirac cone.** Calculated energy difference  $\Delta_{\text{kink}}$  between the asymptotic lines close to the Dirac point of the upper and the lower linear bands vs. doping for suspended graphene (red squares) and for graphene with a model dielectric screening (blue circles) corresponding to the SiC substrate (see Methods). The lines are a guide to the eye.

FIG. 5: **Supplementary Fig. 1: Quasiparticle velocity in graphene.** The slopes (quasi-particle velocity) of the linear bands far from the Dirac point (indicated by the blue dashed lines in Figs. 1c, 1f, and 1i of the manuscript) vs. doping. Red squares and blue circles are calculated quantities for suspended graphene and for graphene with a model silicon carbide (SiC) dielectric screening, respectively. Black triangles are DFT results within the LDA. The lines are a guide to the eye.

FIG. 6: **Supplementary Fig. 2: Calculated dielectric functions of SiC versus energy.** Macroscopic dielectric function of 3C-SiC  $\varepsilon_{0,0}^{\text{SiC}}(\mathbf{q}, \omega)$  versus energy  $\omega$ . Quantities for different wavevectors are shown in different colors. Solid lines and dashed lines show quantities for the wavevector  $\mathbf{q}$  in two representative directions in wavevector space:  $\Gamma$ -X and  $\Gamma$ -L, respectively.